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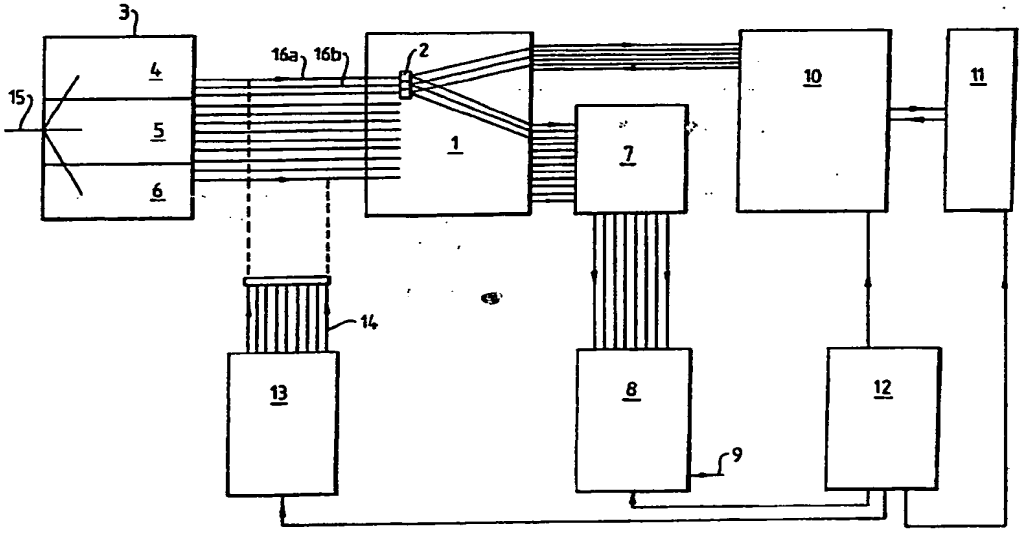
(54) Electrochemical Measurements

(57) In a multi-sensor flow-through apparatus for measuring electrochemically the concentration of a plurality of chemical species in solution, wherein the apparatus comprises a plurality of channels 16a, 16b ... each channel having at least one cell 2 for measuring the preselected species, a digital control means 10, 11 is provided to apply to each cell a preselected potential which is different for at least two cells so that the deposition of a species is varied within a cell. The control means is also adapted to determine the presence and magnitude of each species, and interpret and display the concentration information. In the embodiment relating to anodic stripping voltammetry using a mercury drop technique, the solution to be tested enters at 15 and passes through the reagent system 3 to cells 2, the waste reagent being pumped away 8, 9. Each sample channel 16a, 16b is provided with a valve controlled by means 13 thereby regulating reagents and mercury ions passing to the cells.

Fig.1.



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

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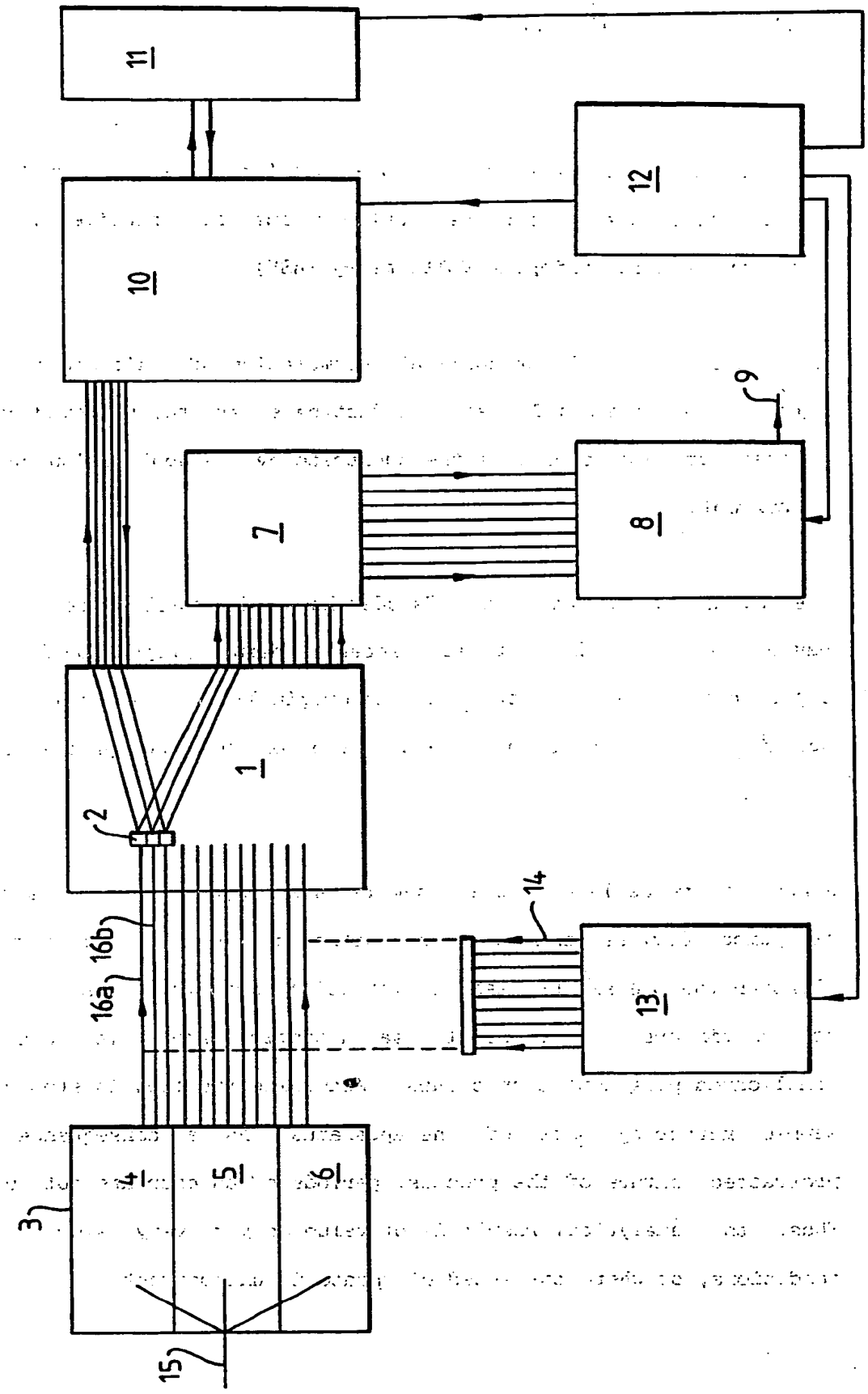

Fig.1.

Digital Control Of A Multi-Sensor System.

The invention relates to an apparatus for digitally controlling a multi-sensor system and particularly, but not exclusively, a system employing Anodic Stripping Voltammetry (ASV).

ASV involves the electrochemical accumulation of ionic species from an aqueous solution sample, at a conducting substrate, followed by removal of that sample species from the substrate by the application or reversal of current.

The ASV method follows simple Faraday laws, the total number of coulombs passed during the removal process being proportional to the concentration of the ionic species originally in the sample. Species specificity is achieved by a selection of the appropriate stripping potential.

Almost universally a discrete sample is employed. However, some anodic stripping devices that have been patented allow for a flowing sample, although the overall process, whilst being periodic in its operation, is not continuous. That is to say a single sample is taken and a complicated programme then ensues. Meanwhile the flow is stopped in the sample gathering part of the apparatus. As a consequence of the protracted nature of the process, periods of an hour are not uncommon. Thus, the analytical result is of value only to very slowly changing conditions, or where the speed of update is unimportant.

Whilst anodic stripping is mainly carried out on solid substrates, improvements with mercury drop polarographic equipment in recent years in the form of the hanging (HMD)/static mercury drop technique has allowed its use in ASV.

Unprecedented sensitivities are now common place with this type of polarographic equipment when applied to ASV. Although somewhat limited to a laboratory bench environment because of its fragile nature, and whilst still mainly restricted to discrete samples, the application of electronic/electrochemical pulsing techniques, prior and during the stripping cycle allows sensitivities to each at least 10^{-10}M for a wide range of inorganic ion and organic species. One such technique is Differential Pulse Anodic Stripping Voltametry (DPASV).

This method has become a competitor for Atomic Absorption Spectroscopy (AAS) in terms of its comparable sensitivity and, more importantly, no sample pre-treatment is usually necessary for DPASV. In addition, when an adsorptive mode is applied, sensitivity may be increased to 10^{-11}M.

Using ASV it is therefore possible to provide a multi-sensor system including a plurality of electrochemical cells wherein each electrochemical cell is adapted to determine the presence and concentration of a chemical species within a sample solution. This is achieved by applying a pre-determined potential to each cell. For each chemical species it will be important to determine the key markers such as deposition, accumulation, reduction and oxidation potentials, flow rate of sample, sweep rate, pulse rate and its magnitude; nature of

signal response, whether curved or linear with concentration, temperature effects, and cross-sensitivities. Once all this information is known, it will be possible to manipulate each sensor cell so that the concentration of a pre-selected chemical species can be identified.

Hitherto, ASV has been undertaken using analogue electronic circuitry means and has typically involved cumbersome and complex circuitry. It is extremely difficult and commercially undesirable to provide an analogue multi-sensor system because the amount of circuitry is prohibitive. We have therefore developed a digital sensor system which uses a conventional PC to control same.

The object of the present invention is to provide a multi-sensor system which ideally, but not exclusively, takes a plurality of readings simultaneously and which is further portable.

According to the present invention there is provided a a digital control means for a multi-sensor flow through apparatus for taking electrochemical measurements to determine the concentration of a plurality of chemical species within a sample solution comprising a plurality of sample channels each channel having therein at least one sample cell, each sample cell being adapted to electrochemically measure the concentration of a pre-selected chemical species wherein there is provided a digital control means which is adapted to:

apply to each sample cell a pre-selected potential whereby the potential applied to at least some of the cells will be different such that the deposition of a pre-selected chemical species on a corresponding electrode will be varied;

determine the presence and magnitude of each chemical species, reduced or oxidized at each electrode;

interpret the information so as to determine the concentration of each pre-selected chemical species at each electrode;

display said concentration information on a display means for an operator to view.

In one realisation of the present invention, the digital control means could further include means for controlling the passage of reagents and particularly mercury ions through the multi-sensor system.

This could be achieved in part by the use at least one valve provided within each sample channel.

Additionally, further digital control means could be provided so that each conduit can be controlled so that mercury ions can be directed to all cells simultaneously for plating purposes.

An apparatus in accordance with the invention is thus under digital control and therefore the circuitry required to manipulate the apparatus can be reduced in size thus reducing considerably the overall size of the apparatus and hence its portability.

An embodiment of the invention will now be described, by way of example only, with reference to the single Figure which is a schematic diagram of a multi-sensor system in accordance with the invention.

The Figure shows a multi-sensor system including a sensor cell bank 1

including a plurality of sensors 2 wherein each sensor 2 is adapted to take a pre-selected ASV reading so as to identify the presence of a pre-selected chemical species within a sample solution. Sensors 2 may be arranged in any preferred array.

Upstream of said sensor system 1 there is provided a reagent system 3 including chambers 4, 5 and 6. Chamber 4 is adapted to allow at least one pre-selected resin access to a sample solution. Chamber 5 is adapted to add at least one pre-selected reagent to a sample solution, for example a buffering reagent so as to control the pH of the sample solution. Chamber 6 is adapted to add at least one pre-selected ligand to the sample solution with a view to facilitating the identification of a ligand specific chemical species.

Downstream of said sensor system 1 there is provided a waste reagent retrieval system 7. System 7 is optional.

Downstream of sensor 1 and/or system 7 there is provided a pump means 8 adapted to pump the sample solution to waste 9.

Electronic circuitry 10 is provided downstream of sensor system 1 and connected thereto such that sampling information from sensors 2 can be accessed and interrogated by computer 11. The combination of the electronic circuitry 10 and the computer 11 form the digital control system for the multi-sensor flow through system.

A power source 12 is provided for operating the electronics 10 and the computer 11 and also the pump 8.

A control means 13 comprising valve means may be provided for controlling the passage of reagents and particularly mercury ions through the system. Where such control means 13 are provided, at least one valve is provided within each sample channel. The valve means are connected by valve control lines 14 to rest of the control means 13. Each conduit is ideally provided with a control means 13 so that mercury ions can be directed to all cells simultaneously for plating purposes.

The multi-sensor apparatus is provided with an inlet comprising a single inlet conduit 15. The conduit 15 enters the reagent system 3 and ideally traces a route that passes through chambers 4,5 and 6 such that the sample solution within the entry conduit 15 is exposed to pre-selected resins, reagents, ligands and the like.

After the sample solution has been supplemented or conditioned, in the aforementioned manner, the resultant sample solution from the reagent system 3 enters a plurality of independent and isolated sample channels 16a, 16b, 16c, 16d.....16nth. Each sample channel 16a, 16b, 16c, 16d.....16nth is provided with a single sample cell 2. Since each sample cell 2 will be adapted to measure, via ASV, the concentration of a pre-selected chemical species within the sample solution, each sample cell 2 will have a characteristic electrochemical signature or requirement. This signature will be determined according to the chemical species to be identified. Thus, each sample solution passing through each sample cell will experience a different imposed electrochemical field. Once a reading has been taken the signal of this reading will pass via an electronic system 10 to the computer 11 where

the reading will be interrogated and interpreted. The results of this process will then be displayed on suitable means for an operator to read.

Sample solution passing through sensor cells 2 remains in sample channels 16a, 16b, 16c, 16d.....16nth and may enter a waste reagent retrieval system 7.

The waste reagent retrieval system 7 may be any conventional system such as the provision of an exchange resins or the like. Alternatively, the techniques used in ASV may be applied for stripping each channel of a pre-selected chemical species. Each channel would be provided with an appropriate electrode and an appropriate potential would be applied to that electrode in order to remove a particular chemical species. This may be repeated in order to remove a plurality of chemical species.

After passage through the independent and isolated sample channels 16a. 16b, 16c, 16d.....16nth and the waste reagent retrieval system 7, the resulting solution can then be passed via pump 9 to a sample waste 9.

Throughout the above, sample channels 16a, 16b, 16c, 16d.....16nth remain isolated and separate.

The sample channels 16a, 16b, 16c, 16d.....16nth can feed into a well, the ends of the sample channels being spaced from the upper most surface of the solution within the well so that the fluid leaving the sample channels, 16a, 16b, 16c,...16nth passes through free space before any mixing occurs within the well. Thus, contact between sample solution in

adjacent sample channels can be avoided until after electrochemical contact between adjacent sample solutions is effectively cut.

computer 11 is programmed to operate the multi-sensor system by applying characteristic electrochemical potentials to each of the sensor cells in order to measure the presence and magnitude of a pre-selected chemical species at each of the sensor cells by conventional ASV. The current flow in response to the applied potential is interpreted by computer 11 to provide a quantitative measurement of a pre-selected chemical species. The sum of the measurements taken can be displayed in graphic form on a conventional monitor screen.

Thus, digital control of a multi-sensor system using ASV techniques is achieved.

Claims

1 Digital control means for a multi-sensor flow through apparatus for taking electrochemical measurements to determine the concentration of a plurality of chemical species within a sample solution comprising a plurality of sample channels, each channel having therein at least one sample cell, each sample cell being adapted to electrochemically measure the concentration of a pre-selected chemical species wherein there is provided digital control means which is adapted to:

a) apply to each sample cell a pre-selected potential, the potential applied to at least two of the sample cells being different so that the deposition of a pre-selected chemical species on an electrode within the corresponding sample cell is varied;

b) determine the presence and magnitude of each chemical species, reduced or oxidized, at each electrode;

c) interpret the information so as to determine the concentration of each pre-selected chemical species at each electrode;

d) display said concentration information on a display means for an operator to view.

2 A digital control means as claimed in claim 1 wherein there is further provided digital control means for controlling the passage of reagents

and particularly mercury ions through the system.

3 A digital control means as claimed in claim 2 wherein the digital control means controls at least one valve provided within each sample channel.

4 A digital control means as claimed in any of the previous claims wherein further digital control means are provided so that each conduit is controlled so that mercury ions can be directed to all cells simultaneously for plating purposes.

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Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

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Relevant Technical Fields

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Search Examiner
Mr J L Freeman

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12 January 1995

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES : WPI, CLAIMS, INSPEC

Documents considered relevant following a search in respect of Claims :-
1 to 4

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	GB 2155185 A	(U S DEPARTMENT OF ENERGY) page 1 line 84	1
X,Y,&	EP 0540974 A	(BAYER A G) column 1 line 7 US 5298146 column 1 line 11	1
Y	EP 0257197 A	(IBM) column 4 lines 20 to 31	1
Y	WO 92/09885 A	(SOLOMAT LTD) pages 1 to 7	1
X,Y	US 5120421	(U S DEPARTMENT OF ENERGY) column 5 lines 33 to 41	1

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